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(54) Method and apparatus for treating wastes by gasification

(57) A method and apparatus for treating wastes by gasification recovers metals or ash content in the wastes in such a state that they can be recycled, and gases containing carbon monoxide (CO) and hydrogen (H₂) for use as synthesis gas of ammonia (NH₃). The wastes are gasified in a fluidized-bed reactor at a relatively low temperature, and gaseous material and char produced in the fluidized-bed reactor are introduced into the high-temperature combustor. The synthesis gas is produced in the high-temperature combustor at a relatively high temperature. CO and H₂O in the synthesis gas is converted into CO₂ and H₂, and then H₂ is recovered by removing CO₂.

Description

BACKGROUND OF THE INVENTION

Field of the Invention:

The present invention relates to a method and apparatus for treating wastes by gasification, and more particularly to a method and apparatus for treating wastes by gasification at a relatively low temperature and then at a relatively high temperature to recover metals or ash content in the wastes in such a state that they can be recycled, and gases containing carbon monoxide (CO) and hydrogen (H₂) for use as synthesis gas of ammonia (NH₃).

Description of the Prior Art:

Ammonia (NH₃) is a basic material for chemical industry which is mass-produced material of nitric acid, various fertilizers; including ammonium nitrate, ammonium sulfate and urea, acrylonitrile, caprolactam or the like. The ammonia is synthesized from nitrogen (N₂) and hydrogen (H₂) under a high pressure in the presence of a catalyst. Hydrogen (H₂) has been produced by either steam reforming of natural gas or naphtha, or partial combustion, i.e. gasification of hydrocarbon such as petroleum, coal or petroleum coke.

It has heretofore been customary to treat organic wastes including municipal wastes, plastic wastes including fiber-reinforced plastics (FRP), biomass wastes, and automobile wastes by incineration to reduce volume thereof, or to discard the organic wastes in an untreated state in landfill sites.

Therefore, a small quantity of useful resources has been recovered from the organic wastes, and used for recycling, irrespective of direct or indirect utilization.

Hydrogen which is a material for ammonia (NH₃) is obtained from natural gas, naphtha, petroleum, coal or petroleum coke. Since most of those materials are dependent on importation from abroad, there have longed for procuring materials which are inexpensive and available in our own country.

On the other hand, the incineration of solid wastes has been disadvantageous for the following reasons:

A stoker furnace or a fluidized-bed furnace has heretofore been used for the incineration of solid wastes. However, this incineration has been problematic in respect to environmental conservation, or recycling of resources or energy. To be more specific, large quantities of exhaust gas are discharged because of high air ratio, and toxic Dioxins are contained in the exhaust gas. Further, metals which are discharged from the furnace are not suitable for recycling because they are oxidized, and landfill sites become scarce year by year. Recently, the number of waste treatment facilities which incorporate ash-melting equipment is increasing, however, a problem is encountered in construction cost and/or operating cost of the waste treatment facilities.

Further, recently, there has been developing a tendency to utilize energy of the solid wastes efficiently.

Dumping the solid wastes in an untreated state on the land has become more difficult because of scarcity of landfill sites, and has not been allowable from the viewpoint of environmental conservation. Therefore, there is no site where the solid wastes such as shredder dust of scrapped cars can be disposed of.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a method and apparatus for treating wastes by gasification which can recover resources in wastes, open up a road to separation and reuse of the resources, produce synthesis gas having desired components for use as synthesis gas of ammonia by partial combustion, solve various problems caused by incineration or dumping of organic wastes, and obtain a low cost hydrogen (H₂) which is used for synthesis of ammonia.

In order to achieve the above object, according to one aspect of the present invention, there is provided a method for treating wastes by gasification, comprising the steps of: gasifying wastes in a fluidized-bed reactor at a relatively low temperature; introducing gaseous material and char produced in the fluidized-bed reactor into a high-temperature combustor; producing synthesis gas in the high-temperature combustor at a relatively high temperature; quenching the synthesis gas produced in the high-temperature combustor; converting CO and H₂O in the synthesis gas into CO₂ and H₂; and recovering H₂ by removing CO₂.

According to another aspect of the present invention, there is provided an apparatus for treating wastes by gasification, comprising: a fluidized-bed reactor for gasifying wastes at a relatively low temperature to produce gaseous material and char; a high-temperature combustor for producing synthesis gas at a relatively high temperature; a quenching chamber containing water for quenching the synthesis gas; a converter for converting CO and H₂O in the synthesis gas into CO₂ and H₂; and an absorber for absorbing CO₂ to recover H₂.

The gasifying steps in the fluidized-bed reactor and the high temperature combustor may be carried out under a pressure ranging from 10 to 40 atm. The recovered H₂ may be used for producing ammonia.

The method may comprise the step of separating air into oxygen and nitrogen, the separated oxygen being used for gasifying agent in the fluidized-bed reactor and the high-temperature combustor, and the separated nitrogen being used for producing ammonia.

The relatively low temperature in a fluidized-bed of the fluidized-bed reactor may be in the range of 450 to 650°C, and temperature in a freeboard of the fluidized-bed reactor may be in the range of 600 to 800°C.

The relatively high temperature in the high-temperature combustor may be 1300°C or higher.

In the gasification process, a mixture of oxygen obtained by separation of air and steam is used as a gasifying agent for producing hydrogen. Nitrogen obtained by separation of air is used for synthesis of ammonia (NH_3). The separation of air into oxygen and nitrogen is carried out by a low-temperature separation method (PSA), an adsorption method (TSA) or a membrane separation. By using oxygen enriched air as a gasifying agent, a mixture of hydrogen (H_2) and nitrogen (N_2) with a ratio of 3 : 1 can be generated, and the generated gas can be used for synthesis of ammonia (NH_3).

The apparatus may further comprise a scrubber provided at the downstream of the quenching chamber for removing dust and toxic gas such as HCl in the generated gas, a CO converter for converting CO and H_2O in the generated gas into H_2 and CO_2 , an acid gas removing device for removing CO_2 and H_2O after the CO shift conversion, and a reactor for reacting the refined H_2 with the refined N_2 to synthesize NH_3 .

Further, it is desirable that the apparatus further comprises a separator for separating air into N_2 and O_2 , means for introducing the separated N_2 into the reactor for synthesizing ammonia (NH_3), and means for introducing the separated O_2 into the fluidized-bed reactor and/or the high-temperature combustor.

The above and other objects, features and advantages of the present invention will become apparent from the following description when taken in conjunction with the accompanying drawings which illustrate preferred embodiments of the present invention by way of example.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic diagram of an apparatus for carrying out the treating method according to a first embodiment of the present invention,

FIG. 2 is a schematic diagram of an apparatus for carrying out the treating method according to a second embodiment of the present invention,

FIG. 3 is a flow diagram showing a process for synthesizing ammonia (NH_3) from the wastes according to an embodiment of the present invention, and FIG. 4 is a graph showing characteristics of pyrolysis in a nitrogen atmosphere of RDF.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

A method and apparatus for treating wastes by gasification according to the present invention will be

The alternative fuels include refuse-derived fuel (RDF) which is produced by pulverizing and classifying municipal wastes, adding quicklime to the classified municipal wastes, and compacting them to shape and solid-water mixture which is produced by crushing municipal wastes, converting them into a slurry with water, and converting it into an oily fuel by hydrothermal reaction. The biomass wastes include wastes generated from water supply or sewage plant (admixture, remnant, sewage sludges, or the like), agricultural wastes (rice husk, rice straw, surplus products, or the like), forestry wastes (sawdust, bark, lumber from thinning, or the like), industrial wastes (pulp-chip dust, or the like), and scrap wood from construction. The low-quality coal includes peat which has low degrees of coalification, or coal refuse which is produced upon coal dressing.

The present invention is also applicable to organic materials including oil shale, garbage, carcasses of beasts, wastes clothing, wastes paper, and any other material.

These wastes are first supplied into a fluidized-bed reactor, pyrolyzed therein. Particularly, by employing a revolving-type fluidized-bed reactor as the reactor, the wastes which have been coarsely crushed by pretreatment can be supplied to the fluidized-bed reactor. The reason is that by a vigorous revolving flow of the fluidized medium, good heat transfer to the supplied wastes can be obtained, and large-sized incombustibles can be discharged from the fluidized-bed furnace. The effects of the revolving flow of the fluidized medium will be described later in detail.

Therefore, among these wastes, the municipal wastes, the biomass wastes, the plastic wastes, and the automobile wastes are roughly crushed to a size of about 30 cm. The sewage sludges and night soil which have a high moisture content are dehydrated into a cake by a centrifugal separator or the like in dedicated treatment facilities, and then the dehydrated cake is transported to a plant site which has a treating system of the present invention. The refuse-derived fuel, the solid water mixture, and the highly concentrated wastewater are used as they are. Coal added for calorie adjustment may be used as it is, if it is crushed to a size of 40 mm or less.

The above wastes may be roughly grouped into high calorific wastes and low calorific wastes according to the calorie of their own and their moisture content. Generally, the municipal wastes, the refuse-derived fuel, the solid water mixture, the plastic wastes, the automobile wastes, and the electric appliance wastes belong to the high calorific wastes. The biomass wastes, the spe-

wastes, including the refuse-derived fuel, the solid water mixture, the plastic wastes, the automobile wastes, low-grade coal, waste oil, and alternative fuels which are produced by solidifying or slurring the above wastes.

These wastes are charged into a high calorific waste pit, a low calorific waste pit, and a tank, and sufficiently stirred and mixed in the pits and the tank. There-

after, they are supplied to the fluidized-bed reactor. Metals contained in the wastes which are supplied to the fluidized-bed reactor are recovered in a non-corroded condition if their melting points are higher than the fluidized-bed temperature in the fluidized-bed reactor. Therefore, these recovered metals can be used as ingot metal in accordance with a kind of metal.

If the wastes supplied to the fluidized-bed reactor have a constant quality, then the ratio of the wastes to the gas supplied to the fluidized-bed reactor for gasification is also constant. However, if the proportion of the low calorific wastes in the supplied wastes increases or the overall moisture content in the supplied wastes increases, then the temperature of the fluidized-bed tends to go down from a desired value. When the temperature of the fluidized-bed goes down, it is desirable to adjust the proportion of the low calorific wastes to the high calorific wastes in the supplied wastes to keep the calorific value of the supplied wastes constant from the viewpoint of gas utilization at a later stage. Alternatively coal with a high calorific value may be added to adjust the calorie of the supplied wastes. Incidentally, oil coke may be added instead of coal to adjust the calorie of the supplied wastes.

Next, a fluidized-bed reactor for gasifying wastes at a relatively low temperature according to the present invention will be described below. Using such a fluidized-bed reactor for gasifying wastes at a relatively low temperature is one of the features of the present invention.

Fluidized-bed reactors themselves are known as combustion or gasification furnaces. However, it is a novel feature of the present invention to use a combination of a fluidized-bed reactor and a high-temperature combustor for producing combustible gases, differently to the prior art.

There is a known technology in which coal is supplied into a high-temperature gasification furnace as pulverized coal or slurried coal with water. However, in case of wastes, it is not easy to pulverize them, compared with coal. Particularly, if the wastes contain incombustibles such as metals, debris, or stones, then it is almost impossible to pulverize the wastes or slurry the wastes. However, in case of using the fluidized-bed reactor, the wastes can be pyrolyzed in a coarsely crushing state to thus generate combustible gaseous materials and fine char. The generated gaseous materials and char are introduced into a subsequent high-temperature combustor in which they are gasified at a relatively high temperature. In the fluidized-bed reactor, only necessary work is to convert the wastes into combustible gaseous materials and char by a slow reaction of thermal decomposition and gasification, thus the fluidized-bed in the fluidized-bed reactor can be kept at a relatively low temperature. The fluidized-bed reactor which can be used in the present invention may be a known atmospheric or pressurized fluidized-bed reactor including a bubbling-type fluidized-bed furnace, in consideration of characteristics of wastes to be treated. However

it is particularly preferable to use a revolving flow-type fluidized-bed reactor which has been developed by the inventors of the present invention.

The revolving flow-type fluidized-bed reactor preferably has a circular horizontal cross-section, and has a relatively mild fluidized-bed with a substantially low fluidizing gas rate in a central region and a relatively intensive fluidized-bed with a substantially high fluidizing gas rate in a peripheral region. The revolving flow-type fluidized-bed reactor has an inclined wall installed along an inner wall in the vicinity of the surface of the fluidized-bed, for deflecting the flow of the fluidized medium from the peripheral region toward the central region so that a revolving flow of the fluidized medium is formed in such a manner that the fluidized medium descends in the mild fluidized-bed, ascends in the intense fluidized-bed, moves from the central region toward the peripheral region in a lower portion of the fluidized-bed and moves from the peripheral region toward the central region in an upper portion of the fluidized-bed.

The revolving flow-type fluidized-bed reactor having a specific structure according to the present invention offers the following advantages:

1. Since the produced char is not accumulated on the fluidized-bed and is dispersed well and uniformly in the fluidized-bed, oxidization of char can be effectively carried out in the fluidized-bed, particularly in the intense fluidized-bed. Heat generated by oxidization of char is transferred to the fluidized medium, and the transferred heat can be effectively used as a heat source for thermal decomposition and gasification at a central portion of the fluidized-bed in the fluidized-bed reactor.
2. Since the fluidized medium whose upward flow is deflected by the inclined wall collides with each other at the central portion of the fluidized-bed in the fluidized-bed reactor, char is pulverized. If hard silica sand is used as a fluidized medium, pulverization of char is further accelerated.
3. Since the wastes go down into the fluidized-bed by descending flow of the fluidized medium, the solid wastes which have been coarsely crashed only can be supplied to the fluidized-bed reactor. Therefore, it is possible to dispense with a pulverizing equipment, and electric power for pulverizing can be remarkably reduced.
4. Although large-sized incombustibles are generated due to coarse crushing of the wastes, such large-sized incombustibles can be easily discharged by the revolving flow of the fluidized medium from the fluidized-bed reactor.
5. Since the generated heat is dispersed by the revolving flow of the fluidized medium which is formed in overall regions of the fluidized-bed, trouble caused by generation of agglomeration or clinker can be avoided.

In case of a bubbling-type fluidized-bed which is

generally used, although the fluidized medium can be uniformly fluidized in the fluidized-bed, dispersion of the fluidized medium in horizontal directions is not carried out well. Therefore, the revolving flow-type fluidized-bed reactor of the present invention is superior to the bubbling-type fluidized-bed reactor which is commonly used, in respect to the above advantages 1 through 5.

The fluidized-bed reactor of the present invention has the fluidized-bed whose temperature is in the range of 450 to 800°C. If the fluidized-bed temperature is lower than 450°C, since the reaction of thermally decomposing and gasifying the wastes would be extremely slow, undecomposed substances would be accumulated in the fluidized-bed, and an amount of produced char whose oxidation rate is slow would be increased. If the fluidized-bed temperature increases, the pyrolysis reaction of the wastes is speeded up, thereby solving the problem of the accumulation of undecomposed substances in the fluidized-bed. However, fluctuations in the feeding rate of wastes result in fluctuations in the amount of generated gas which would impair the operation of a subsequent swirling-type high-temperature combustor. This is because it is impossible to finely adjust the amount of gas supplied to the swirling-type high-temperature combustor in accordance with the amount of oxygen containing gas generated in the fluidized-bed reactor. Therefore, an upper limit for the temperature in the fluidized-bed is set to 650°C so that the pyrolysis reaction is relatively sluggish. The fluidized-bed reactor has a larger diameter portion above the fluidized-bed which is called "freeboard". By supplying oxygen containing gas such as substantially pure oxygen or oxygen enriched air to the freeboard, the load in the subsequent high-temperature combustor can be reduced, and gasification of tar and char in the generated gas can be accelerated in the freeboard.

According to the present invention, a primary combustion of the wastes is carried out in the fluidized-bed at a temperature ranging from 450 to 650°C, and then a secondary combustion of the wastes is carried out in the freeboard at a temperature ranging from 600 to 800°C, preferably ranging from 650 to 750°C.

The fluidizing gas supplied to the fluidized-bed reactor for gasifying the wastes is selected from air, oxygen enriched air, a mixture of air and steam, a mixture of oxygen enriched air and steam, and a mixture of oxygen and steam. As a fluidized medium, sand such as silica sand or Olivine sand, alumina, iron powder, limestone, dolomite, or the like may be used.

The gases generated in the fluidized-bed reactor contain a large amount of tar and carbonous materials

those whose melting points are lower than the gasification temperature. Therefore, in order to recover aluminum having a melting point of 650°C, it is necessary to set the temperature in the fluidized-bed to 650°C or less.

Next, the reason why the fluidized-bed in the fluidized-bed reactor is kept at a temperature ranging from 450 to 650°C will be described below.

FIG. 4 shows the characteristics of pyrolysis in a nitrogen atmosphere of RDF. In a primary gasification process carried out in the fluidized-bed reactor, it is desirable to generate gaseous components including gas and tar as much as possible and solid components including combustible materials and ash content, that is carbonous materials, as little as possible. Char which is generated from carbonous materials in the fluidized-bed reactor and has a small diameter, is conveyed to the high-temperature combustor with an upward flow of the generated gas in the fluidized-bed reactor, but carbonous materials having a large diameter which have not been crushed well in the fluidized-bed are discharged with incombustibles from the bottom of the reactor.

If the rate of the carbonous materials is high, then the amount of the carbonous materials discharged from the bottom of the reactor must be increased to prevent the solid components from being accumulated in the fluidized-bed. Char discharged from the reactor is reused after removing sand and incombustibles therefrom, but it is desirable to reduce the amount of char discharged from the reactor.

As shown in FIG. 4, as the temperature of thermal decomposition decreases the amount of the generated solid components increases. Further, the speed of thermal decomposition becomes extremely slow at a temperature of 450°C or less, and undecomposed materials tend to be accumulated on the fluidized-bed, and hence operation of the fluidized-bed reactor becomes difficult. Conversely, as the temperature in the fluidized-bed increases, the amount of the generated solid component decreases, thus accelerating pyrolysis of the wastes.

However, since the wastes are supplied to the fluidized-bed reactor in almost non-crushed condition, if possible, reaction velocity increases when the fluidized-bed temperature rises excessively. Therefore, fluctuations in the supplied rate of wastes result in fluctuations in the rate of generated gas and internal pressure of the furnace which would impair the operation of a subsequent high-temperature combustor. It is confirmed by the experiments of gasification using shredder dust of automobile wastes that if gasification temperature is 650°C or less, CO content in the exhaust gas is suppressed to about 10%. Most of the wastes contain

metals. In the fluidized-bed reactor, metals in the wastes can be discharged in a non-corroded condition from the fluidized-bed reactor. The metals which can be recovered are limited to

aluminum, iron, and steel. In order to recover aluminum having a melting point of 660°C, it is necessary to set the temperature in the fluidized-bed to 650°C or less.

Inasmuch as the fluidized-bed reactor is used to gasify wastes at a relatively low temperature, it is possible to treat various wastes having a size in the range of several millimeters to several centimeters. The fluidized-bed reactor has a high capacity and scale-up can be done easily. The fluidized-bed reactor is free of moving parts so that it can easily be operated for adjustment of the temperature and other parameters, and has good thermal conductivity for a heating medium to keep the temperature of the fluidized-bed uniform.

If the fluidized-bed reactor comprises a revolving flow-type fluidized-bed reactor, the wastes do not need to be crushed before being charged into the fluidized-bed reactor. The carbonous materials are effectively crushed in the fluidized-bed into char which is well dispersed in the fluidized-bed, and thus the fluidized-bed reactor has a high capacity of the wastes, can keep temperature in the fluidized-bed uniform, and has a high gasification efficiency.

Next, a high-temperature combustor will be described below. The high-temperature combustor is supplied with gaseous material and char introduced from the fluidized-bed reactor, and gasifies the gaseous material and char at a temperature of 1300°C or higher by being contacted with gas supplied to the high-temperature combustor. Tar and char are fully gasified, and ash content therein is discharged as molten slag from the bottom of the high-temperature combustor.

The high-temperature combustor may comprise a Texaco furnace in which gaseous material and char are blown therein only from an upper part of the furnace, but may preferably comprise a swirling-type high-temperature combustor. In the swirling-type high-temperature combustor, gaseous material and char are gasified at a relatively high temperature while forming a swirling flow with gas for gasification, and ash content is melted, and then molten ash is separated and discharged therefrom.

By using the swirling-type high-temperature combustor, high load combustion and high speed combustion can be performed, distribution of the residence time of gas becomes narrow, a carbon conversion efficiency and a slag mist collecting efficiency are high, and the volume of the combustor may be small.

The gas introduced into the high-temperature combustor for gasification may be selected from oxygen enriched air and oxygen. The total amount of oxygen supplied to the fluidized-bed reactor and the high-temperature combustor may be in the range of 0.1 to 0.6 of the theoretical amount of oxygen for combustion of the wastes. The amount of oxygen supplied to the fluidized-bed reactor may be in the range of 0.1 to 0.3 of the theoretical amount of oxygen for combustion of the wastes. In this manner, fuel gas having a low calorie ranging from 1000 to 1500 kcal/Nm³ (dry) or fuel gas having a medium calorie ranging from 2500 to 4500 kcal/Nm³ (dry) can be obtained from the high-temperature combustor. According to the present invention, gas containing CO and H₂ as main component can be produced from the wastes, and the produced gas can be used as

industrial fuel gas or synthesis for chemical industry.

Since ash content in char which is introduced into the subsequent high-temperature combustor from the fluidized-bed reactor is melted into slag in the high-temperature combustor, harmful heavy metals are fixed in the slag and will not be eluted out. Dioxins and precursor thereof, and PCB (polychlorinated biphenyl) are almost fully decomposed by the high-temperature combustion in the high-temperature combustor.

Generally, in case of producing synthesis gas for use as synthesis for chemical industry, gasification is carried out under a pressure ranging from 10 to 40 atm. However, gasification may be carried out under atmospheric pressure, and refinement of the generated gas may be carried out under a pressure ranging from 30 to 40 atm after a CO conversion. As a gasifying agent used in the fluidized-bed reactor, a mixture of pure oxygen (O₂) obtained by low-temperature separation of air and steam is generally used, but CO₂ recovered by an acid gas removing process may be added to O₂. Nitrogen obtained by low-temperature separation of air is used in synthesis of ammonia (NH₃). Alternatively, oxygen enriched air may be used as a gasifying agent. By adjusting oxygen concentration so that the ratio of H₂ to N₂ is 3 : 1 after the CO conversion, it is possible to use the produced gas as synthesis gas of ammonia as they are. However, this method has disadvantages that flow rate of gas increases, resulting in a large-sized gas treatment equipment.

In case of using wastes as synthesis gas of ammonia, it is necessary to ensure the amount of waste and to make the quality of the wastes stable. Further, it is necessary to deal with change in the quality of the wastes during operation of the system.

In order to solve the above problems according to the present invention, when the system cannot be operated stably only by using the wastes or the system is in start-up, solid fuel such as coal or oil coke having a high calorie and a stable property which is actually used for producing H₂ may be added to the wastes. That is, by adding coal or oil coke to the wastes so that it is contained in the wastes at a rate of 20 to 40%, materials for gasification can be made stable both in quality and in quantity. When the quality of the wastes is lowered due to some cause during operation, and the concentration of H₂ or CO in the gas is lowered, the property of gas can be made stable by increasing a supply rate of the solid fuel. Incidentally, coal used in the system is not low-grade coal which belongs to the wastes but a sub-bituminous coal or bituminous coal having high degrees of coalification.

Various apparatuses for carrying out the method for treating wastes by gasification according to the present invention will be described below with reference to drawings.

FIG. 1 schematically shows an apparatus for carrying out the method for treating wastes by gasification according to a first embodiment of the present invention.

The apparatus shown in FIG. 1 includes a hopper 1, a screw feeder 2, and a revolving flow-type fluidized-bed reactor 3 having a fluidized-bed 4 therein. The fluidized-bed reactor 3 has a freeboard 5 and a burner 6, and is connected to a trommel 7 which is associated with a bucket conveyor 8. The apparatus further includes a swirling-type high-temperature combustor 9 having a primary combustion chamber 10, a secondary combustion chamber 8 and a slag separation chamber 12. The swirling-type high-temperature combustor 9 has burners 13. In FIG. 1, the symbols a, b, b' and c represent organic wastes, air for the fluidized-bed 4, air for the freeboard 5, air for the high-temperature combustor 9, and large-sized incombustibles, respectively. Further, the symbols d, e, e' and f represent silica sand, generated gas, combustion exhaust gas, and slag, respectively.

Wastes "a" are supplied to the hopper 1, and then supplied at a constant rate by the screw feeder 2 to the fluidized bed reactor 3. Air "b" is introduced as a gasifying agent into the fluidized-bed reactor 3 from a bottom thereof, forming a fluidized-bed 4 of the fluidized medium made of silica sand over a dispersion plate in the fluidized-bed reactor 3.

The fluidizing gas having a relatively low fluidizing gas velocity is supplied into the central part of the fluidized-bed 4, and the fluidizing gas having a relatively high fluidizing gas velocity is supplied into the peripheral part of the fluidized-bed 4, thus forming revolving flows of the fluidized medium in the fluidized-bed reactor 4 as shown in FIG. 1.

The organic wastes "a" are charged into the fluidized-bed 4, contacted with O_2 in the air within the fluidized-bed 4 which is kept at a temperature ranging from 450 to 650°C, and quickly pyrolyzed. The fluidized medium in the fluidized-bed 4 and incombustibles are discharged from the bottom of the fluidized-bed reactor 3 and enter the trommel 7 by which the incombustibles "c" are removed. The separated silica sand "d" is charged back through the bucket conveyor 8 into the fluidized-bed reactor 3 from an upper end thereof. The discharged incombustibles "c" contain metals. Since the fluidized-bed 4 is kept at a temperature ranging from 450°C to 650°C, iron, copper and aluminum can be recovered in a non-corroded condition suitable for recycling.

When the wastes "a" are gasified in the fluidized-bed 4, gas, tar and carbonous materials are generated. The gas and tar are atomized and ascend in the fluidized-bed reactor 3. The carbonous materials are pulverized into char by a stirring action of the fluidized-bed 4. Since the char is porous and light, it is carried with the

gasification of tar and char.

The generated gas "e" discharged from the fluidized-bed reactor 3 is supplied into the primary combustion chamber 10 of the swirling-type high-temperature combustor 9, and combusted at a high temperature 1300°C or higher while being mixed with preheated air "b'" in a swirling flow thereof. The combustion is completed in the secondary combustion chamber 11, and the generated exhaust gas "e'" is discharged from the slag separation chamber 12. Because of the high temperature in the swirling-type high-temperature combustor 9, ash content in the char is converted into slag mist which is trapped by molten slag phase on an inner wall of the primary combustion chamber 10 under the centrifugal forces of the swirling flow. The molten slag flows down on the inner wall and enters the secondary combustion chamber 11, from which slag "f" is discharged through a bottom of the slag separation chamber 12. The primary and secondary combustion chambers 10 and 11 are provided with the respective burners 13 for start-up. In this manner, combustion is carried out at an air ratio of about 1.3, and melting of ash content and forming of slag thereof are carried out.

FIG. 2 shows an apparatus for carrying out the method for treating wastes by gasification according to a second embodiment of the present invention.

The apparatus shown in FIG. 2 serves to produce synthesis gas having a high pressure ranging from 10 to 40 atm.

The apparatus comprises a revolving flow-type fluidized-bed reactor 3 and a swirling-type high-temperature combustor 17. The fluidized-bed reactor 3 is connected to a rock hopper 14 which is associated with a screen 15. The swirling-type high-temperature combustor 17 is also connected to a rock hopper 14' which is associated with a screen 15'. The screen 15 is connected to the fluidized-bed reactor 3 through a fluidized medium circulation line 16. The swirling-type high-temperature combustor 17 has a high-temperature gasification chamber 18 and a quenching chamber 19 therein. The swirling-type high-temperature combustor 17 is connected to a cyclone 20 which is connected to a scrubber 21. A settler 22 which is associated with the high-temperature combustor 17 is provided. In FIG. 2, "a'" represents coal or oil coke for supplementary fuel, "g" and "g'" represent a mixture of O_2 and H_2O as a gasifying agent, and "g'" represents O_2 as a gasifying agent.

Wastes "a" are supplied at a constant rate through a rock hopper or the like to the fluidized-bed reactor 3. A mixture of O_2 and H_2O is introduced as a gasifying agent "g" into the fluidized-bed reactor 3 from a bottom thereof, forming a fluidized-bed 4 of the fluidized

medium. The wastes "a" are gasified in the fluidized-bed 4, and the gas, tar and char at a temperature ranging from 500°C to 800°C are thereby accelerating conversion of gas components into low molecular components and

the gas, tar and char are carried upwardly by the gasifying agent "g" within the fluidized-bed 4 which is kept at a temperature ranging from 450 to 650°C and under a pressure ranging from 10 to 40 atm, and are rapidly

pyrolyzed. The fluidized medium in the fluidized-bed 4 and incombustibles are discharged from the bottom of the fluidized-bed reactor 3, pass through the rock hopper 14, and then are supplied to the screen 15 by which the incombustibles "c" are separated. The silica sand "d" is charged back through the fluidized medium circulation line 16 into the fluidized-bed reactor 3. The discharged incombustibles "c" contain metals. Since the fluidized-bed 4 is kept at a temperature ranging from 450 to 650°C, iron, copper and aluminum can be recovered in a non-corroded condition suitable for recycling.

When the wastes "a" are gasified in the fluidized-bed 4, gas, tar and carbonous materials are generated. The gas and tar are vaporized and ascend in the fluidized-bed reactor 3. The carbonous materials are pulverized into char by a vigorous revolving action of the fluidized-bed 4. Since the char is porous and light, it is carried with the upward flow of the generated gas. Since the fluidized medium of the fluidized-bed 4 comprises hard silica sand, the pulverization of the carbonous materials is accelerated. A gasifying agent "g" comprising a mixture of O_2 and H_2O is blown into the freeboard 5 to gasify the gas, tar and char at a temperature ranging from 600 to 800°C for thereby accelerating conversion of gas components into low-molecular components and gasification of tar and char.

The generated gas "e" discharged from the fluidized-bed reactor 3 is supplied into the high-temperature gasification chamber 18 of the swirling-type high-temperature combustor 17, and combusted at a high temperature 1300°C or higher while being mixed with preheated gasifying agent "g" in a swirling flow thereof. Because of the high temperature in the swirling-type high-temperature combustor 17, ash content in the gas is converted into slag mist which enters the quenching chamber 19 with the gas to be contacted with water directly. In the quenching chamber 19, the slag is quenched into granulated slag, and the granulated slag is discharged through the rock hopper 14' to the outside of the high-temperature combustor 17, and then classified into coarse grain slag "f'" and fine grain slag "f'" by the screen 15'.

The generated gas is discharged from the high-temperature combustor 17, and supplied to the scrubber 21 through the cyclone 20. In the scrubber 21, the gas is scrubbed to thus produce refined gas.

FIG. 3 is a flow diagram showing a process for synthesizing ammonia (NH_3) from organic wastes according to an embodiment of the present invention.

As shown in FIG. 3, the process comprises a step 100 of gasification, a step 200 of carbon monoxide conversion, a step 300 of removing acidic gas, a step 400 of gas refining with liquid nitrogen, a step 500 of synthesizing ammonia, and a step 600 of recovering sulfur. An apparatus for carrying out the above process includes a gas scrubber 21, a low-temperature air separator 23, a fluidized-bed reactor 3 for carrying out a primary gasification of organic wastes, a high-temperature combustor 17 for carrying out a secondary gasification at a rela-

tively high temperature, a carbon monoxide converter 36, an absorption tower 40, a condensate tank 41, a carbon dioxide stripping tower 44, a hydrogen sulfide stripping tower 50, an adsorption tower 53, a liquid nitrogen cleaning tower 56, and a cooler 57. The apparatus further includes a compressor 58 for compressing gaseous nitrogen, a compressor 59 for compressing gaseous oxygen, a compressor 60 for compressing synthesis gas, an ammonia synthesis tower 62, an ammonia refrigerator 68, an ammonia separator 70, and an ammonia storage tank 72. The apparatus further includes heat exchangers 38, 39, 48, 52, 64 and 66, and pumps 30, 46 and 54. In FIG. 3, the symbols i, j, q and r represent air, oxygen (O_2), sulfur (S) and ammonium sulfite, respectively.

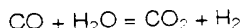
Air "i" is separated into oxygen "j" and nitrogen "k" by the air separator 23. The separated oxygen is compressed by the compressor 59, and supplied to the fluidized-bed reactor 3 and the high-temperature combustor 17 as a gasifying agent. The nitrogen "k" is compressed by the compressor 58, and used as gas for synthesis of ammonia. A low-temperature separation method is generally used for separating air.

In the gasification step 100, organic wastes "a" and a supplementary material "a'" are treated at a relatively low temperature in the fluidized-bed reactor 3, and then treated in the high-temperature combustor 17 at a temperature ranging from 1200 to 1500°C and under a pressure ranging from 10 to 40 kg/cm² G to generate gas containing CO, H_2 , H_2O and CO as main components. The temperature in the high-temperature combustor 17 is mainly adjusted by controlling the amount of oxygen. The high-temperature combustor 17 is of a direct-quench system, and has a high-temperature gasification chamber 18 at an upper part thereof and a quenching chamber 19 at a lower part thereof. The generated gas is quenched in direct contact with a water in the quenching chamber 19, and then discharged from the high-temperature combustor 17. By this quenching, a large amount of steam is generated, the generated steam flows with the generated gas, and most of slag generated in the high-temperature gasification chamber 18 is removed. The slurry of the slag and water is supplied to a slag treatment process. The generated gas, which is accompanied by the large amount of steam when being discharged from the quenching chamber 19, is cleaned in a venturi scrubber (not shown) and the gas scrubber 21 to remove the slag mist therefrom. Thereafter, the generated gas is supplied to the step 200 of carbon monoxide conversion. The scrubbing water in the bottom of the gas scrubber 21 is mainly supplied to the quenching chamber 19 by the pump 30 for circulation, and the part of the scrubbing water is supplied to the slag treatment process.

In the step 200 of carbon monoxide conversion, the generated gas containing steam and supplied from the step 100 of gasification is used as synthesis gas. The gas from the gas scrubber 21 is heated by the heat exchange with a gas passing through a first-stage cata-

lyst bed to a temperature suitable for the carbon monoxide conversion in the heat exchanger 38, and then supplied to the carbon monoxide converter 36. In the carbon monoxide converter 36, carbon monoxide (CO) in the gas reacts with the accompanied steam in the presence of carbon monoxide conversion catalyst to produce hydrogen (H₂). The carbon monoxide converter 36 comprises two-stage catalyst beds composed of Co-Mo catalyst. The temperature at an inlet of the first-stage catalyst bed is approximately 300°C. The molar ratio of steam to dry generated gas is approximately 1.5. The temperature at an exit of the first-stage catalyst bed is not allowed to exceed 480°C.

The temperature at an inlet of the second-stage catalyst bed is approximately 300°C. The conversion ratio is 90% or more, and the concentration of carbon monoxide in the dry gas at the exit of the carbon monoxide converter 36 is 2% or less. The carbon monoxide conversion reaction is expressed by the following formula:



This reaction is exothermic reaction, and the high-temperature gas passing through the first-stage catalyst bed is cooled by the heat exchange with a gas from the inlet of the carbon monoxide converter 36, and then enters the second-stage catalyst bed. In the second-stage catalyst bed, the carbon monoxide conversion reaction proceeds furthermore.

The gas passing through the carbon monoxide converter 36 is cooled by the heat exchanger 39 to approximately 40°C, and separated in the condensate tank 41 into condensed water and gas, and then cooled to -17°C by the heat exchange with a part of purified gas from the top of the nitrogen cleaning tower 56. Thereafter, the cooled gas is supplied to the step 300 of removing acidic gas in which a physical adsorption process, i.e. Rectisol process, is carried out to remove impurities including hydrogen sulfide (H₂S), carbonyl sulfide (COS) and carbon dioxide (CO₂), from the converted gas supplied from the step 200 of carbon monoxide conversion.

The gas cooled to -17°C is introduced into the absorption tower 40 in which carbon dioxide (CO₂) is absorbed by being contacted with liquid methanol of approximately -60°C countercurrently. As a result, the gas discharged from the absorption tower 40 contains carbon dioxide (CO₂) concentration ranging from 10 to 20 ppm and hydrogen sulfide (H₂S) concentration of approximately 0.1 ppm. As methanol used as an absorption liquid absorbs carbon dioxide, the tempera-

ture of the absorption tower 40. In order to recover hydrogen (H₂) and carbon monoxide (CO) from the methanol, the methanol is treated under reduced pressure in a methanol regeneration tower (not shown) to release hydrogen (H₂) and carbon monoxide (CO) therefrom. The released hydrogen and carbon monoxide are compressed by a compressor, and used for recirculation. On the other hand, in order to recover carbon dioxide (CO₂) of high purity which is absorbed by the methanol, the methanol is supplied to the carbon dioxide stripping tower 44, and depressurised therein and stripped by gaseous nitrogen, whereby carbon dioxide (CO₂) in the methanol is released and the released carbon dioxide is recovered.

The methanol containing condensed hydrogen sulfide (H₂S) is taken out from the bottom of the carbon dioxide stripping tower 44 and supplied to the heat exchanger 48 by the pump 46. After heated in the heat exchanger 48, the methanol is supplied to the hydrogen sulfide stripping tower 50 in which it is indirectly regenerated by steam. Hydrogen sulfide enriched gas discharged from the top of the hydrogen sulfide stripping tower 50 is cooled in the heat exchanger 52, and then supplied to the step 600 of recovering sulfur in which sulfur "q" or ammonium sulfite "r" is recovered. The methanol drawn from the bottom of the hydrogen sulfide stripping tower 50 is supplied to the top of the absorption tower 40 by the pump 54 for recirculation.

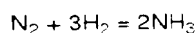
Hydrogen enriched gas supplied from the absorption tower 40 which contains a small amount of carbon monoxide (CO) and a trace amount of carbon dioxide (CO₂) passes through the adsorption tower 53 to allow methanol and carbon dioxide to be removed therein, and is cooled to approximately -190°C by the cooler 57, and then supplied to the liquid nitrogen cleaning tower 56. In the step 400 of gas refining with liquid nitrogen, the supplied gas containing a trace amount of carbon monoxide (CO) and methane (CH₄) is cleaned with supercooled liquid nitrogen to thereby remove carbon monoxide and methane. Gaseous hydrogen is not absorbed by the liquid nitrogen because hydrogen has a lower boiling point than nitrogen. Therefore, purified hydrogen enriched gas containing nitrogen is obtained from the top of the nitrogen cleaning tower 56.

The purified gas discharged from the top of the liquid nitrogen cleaning tower 56 is mixed with gaseous nitrogen having high pressure which is generated from the liquid nitrogen cooled by the cooler 57 so that the molar ratio of hydrogen to nitrogen is adjusted to a suitable value, i.e., approximately 3 suitable for ammonia synthesis, and the mixed gas is heated through the cooler 57 again and supplied to the step 500 for synthesis of ammonia.

Small amount of Hydrogen (H₂) and carbon monoxide (CO) in addition to carbon dioxide (CO₂) and hydrogen sulfide (H₂S) are dissolved in the methanol drawn

from the bottom of the nitrogen cleaning tower 56 countercurrently, and impurities including carbon monoxide (CO), argon (Ar) and methane (CH₄) in the

supplied gas are absorbed with liquid nitrogen, and removed. The liquid nitrogen which has absorbed the impurities such as carbon monoxide (CO), argon (Ar) and methane (CH₄) is drawn from the bottom of the nitrogen cleaning tower 56, and depressurized and used as a fuel for a boiler. The gas supplied from the cleaning step 400 is compressed to a pressure of, for example, 150 kg/cm²G in the first-stage of the compressor 60, and then the compressed gas is mixed with the recirculating gas from the ammonia separator 70. Thereafter, the mixed gas is compressed to a pressure of 165 kg/cm²G in the second-stage of the compressor 60, and then supplied to the ammonia synthesis tower 62. The ammonia synthesis tower has two-stage catalyst beds composed of Fe catalyst. The gas at an inlet of the ammonia synthesis tower 62 has a pressure of 164 kg/cm² and a temperature of 250°C. The ammonia synthesis reaction is carried out when the synthesis gas passes through the catalyst beds. The reaction is expressed by the following formula:



The gas which has passed through the catalyst beds has a temperature exceeding 500°C, however, it is cooled by the cooled gas introduced into the ammonia synthesis tower 62.

The ammonia discharged from the ammonia synthesis tower 62 has a pressure of 160 kg/cm²G and a temperature of 450°C. The ammonia is cooled to around room temperature by the heat exchangers 64 and 66, and further cooled by the ammonia refrigerator 68, thus most of ammonia is condensed. The condensed ammonia is separated into liquid ammonia and gas, and the liquid ammonia is fed to the ammonia storage tank 72. The separated gas is supplied to the second-stage of the compressor 60 by which it is compressed to a pressure of 165 kg/cm²G, and then the compressed gas is supplied to the ammonia synthesis tower 62 for recirculation.

As described above, the method and apparatus for treating wastes by gasification according to the present invention offers the following advantages:

1. Hydrogen which is a material for ammonia (NH₃) can be produced from organic wastes which are available in our own country. Thus, production cost of ammonia is greatly reduced.
2. By gasifying the organic wastes to produce hydrogen, various problems caused by conventional incineration treatment can be solved. To be more specific, the amount of exhaust gas is greatly reduced, and dioxins and precursor thereof are not generated. Further, since ash content in the wastes is converted into harmless slag, a life of reclaimed land can be prolonged, and the recovered slag can be utilized as pavement materials.
3. Metals such as iron, copper or aluminum can be recovered in a non-corroded condition suitable for

recycling

From the viewpoint of effective utilization of the wastes and environmental conservation, gasification facilities for gasifying organic wastes and ammonia synthesis facilities are constructed adjacently to each other, and combined organically in respect to utilization of materials to enhance functions of both of facilities as a total system.

4. By supplying supplementary fuel such as coal or oil coke, it is possible to deal with fluctuations of the wastes both in quality and in quantity. Particularly, the gasification facilities can be operated stably against deterioration in property of produced gas by increasing mixing ratio of the solid fuel.

Although certain preferred embodiments of the present invention have been shown and described in detail, it should be understood that various changes and modifications may be made therein without departing from the scope of the appended claims.

According to its broadest aspect the invention relates to:

A method for treating wastes by gasification, comprising the steps of:
 gasifying wastes in a fluidized-bed reactor at a relatively low temperature;
 introducing gaseous material and char produced in said fluidized-bed reactor into a high-temperature combustor; and
 producing synthesis gas in said high-temperature combustor at a relatively high temperature.

It should be noted that the objects and advantages of the invention may be attained by means of any compatible combination(s) particularly pointed out in the items of the following summary of the invention and the appended claims.

SUMMARY OF THE INVENTION:

1. A method for treating wastes by gasification, comprising the steps of:

gasifying wastes in a fluidized-bed reactor at a relatively low temperature;
 introducing gaseous material and char produced in said fluidized-bed reactor into a high-temperature combustor;
 producing synthesis gas in said high-temperature combustor at a relatively high temperature;
 quenching said synthesis gas produced in said high-temperature combustor;
 converting CO and H₂O in said synthesis gas into CO₂ and H₂; and recovering H₂ by removing CO₂.

2. A method wherein said gasifying steps in said fluidized-bed reactor and said high temperature combustor are carried out under a pressure ranging

from 10 to 40 atm.

3. A method wherein said recovered H_2 is used for producing ammonia.

4. A method further comprising separating air into oxygen and nitrogen, the separated oxygen being used for gasifying agent in said fluidized-bed reactor and said high-temperature combustor, and the separated nitrogen being used for producing ammonia.

5. A method wherein said relatively low temperature in a fluidized-bed of said fluidized-bed reactor is in the range of 450 to 650°C, and temperature in a freeboard of said fluidized-bed reactor is in the range of 600 to 800°C.

6. A method wherein said relatively high temperature in said high-temperature combustor is 1300°C or higher.

7. An apparatus for treating wastes by gasification, comprising:

a fluidized-bed reactor for gasifying wastes at a relatively low temperature to produce gaseous material and char;

a high-temperature combustor for producing synthesis gas at a relatively high temperature;

a quenching chamber containing water for quenching said synthesis gas;

a convertor for converting CO and H_2O in said synthesis gas into CO_2 and H_2 ; and

an absorber for absorbing CO_2 to recover H_2 .

8. An apparatus according to claim 7, wherein gasifications in said fluidized-bed reactor and said high-temperature combustor are carried out under a pressure ranging from 10 to 40 atm.

9. An apparatus wherein said recovered H_2 is used for producing ammonia.

10. An apparatus further comprising a separator for separating air into oxygen and nitrogen, the separated oxygen being used for gasifying agent in said fluidized bed reactor and said high-temperature combustor, and the separated nitrogen being used for producing ammonia.

11. An apparatus wherein said relatively low tem-

perature is 450 to 650°C.

12. An apparatus wherein said relatively high temperature in said high-temperature combustor is

1300°C or higher.

Claims

1. A method for treating wastes by gasification, comprising the steps of:

gasifying wastes in a fluidized-bed reactor at a relatively low temperature;

introducing gaseous material and char produced in said fluidized-bed reactor into a high-temperature combustor;

producing synthesis gas in said high-temperature combustor at a relatively high temperature;

quenching said synthesis gas produced in said high-temperature combustor;

converting CO and H_2O in said synthesis gas into CO_2 and H_2 ; and

recovering H_2 by removing CO_2 .

2. A method according to claim 1, wherein said gasifying steps in said fluidized-bed reactor and said high temperature combustor are carried out under a pressure ranging from 10 to 40 atm.

3. A method according to claim 1, wherein said recovered H_2 is used for producing ammonia.

4. A method according to claim 3, further comprising separating air into oxygen and nitrogen, the separated oxygen being used for gasifying agent in said fluidized-bed reactor and said high-temperature combustor, and the separated nitrogen being used for producing ammonia.

5. A method according to claim 1, wherein said relatively low temperature in a fluidized-bed of said fluidized-bed reactor is in the range of 450 to 650°C, and temperature in a freeboard of said fluidized-bed reactor is in the range of 600 to 800°C.

6. A method according to claim 1, wherein said relatively high temperature in said high-temperature combustor is 1300°C or higher.

7. An apparatus for treating wastes by gasification, comprising:

a fluidized-bed reactor for gasifying wastes at a relatively low temperature to produce gaseous material and char;

a high-temperature combustor for producing synthesis gas at a relatively high temperature;

a quenching chamber containing water for quenching said synthesis gas;

a convertor for converting CO and H_2O in said synthesis gas into CO_2 and H_2 ; and

an absorber for absorbing CO_2 to recover H_2 .

8. An apparatus according to claim 7 wherein gasifications in said fluidized-bed reactor and said high-temperature combustor are carried out under a pressure ranging from 10 to 40 atm.

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9. An apparatus according to claim 7 or 8, wherein preferably said recovered H_2 is used for producing ammonia,

and/or further preferably comprising a separator for separating air into oxygen and nitrogen, the separated oxygen being used for gasifying agent in said fluidized-bed reactor and said high-temperature combustor, and the separated nitrogen being used for producing ammonia,

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and/or wherein preferably said relatively low temperature in a fluidized-bed of said fluidized-bed reactor is in the range of 450 to 650°C, and temperature in a freeboard of said fluidized-bed reactor is in the range of 600 to 800°C, and/or

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wherein preferably said relatively high temperature in said high-temperature combustor is 1300°C or higher.

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10. A method for treating wastes by gasification, comprising the steps of:

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gasifying wastes in a fluidized-bed reactor at a relatively low temperature;

introducing gaseous material and char produced in said fluidized-bed reactor into a high-temperature combustor;

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producing synthesis gas in said high-temperature combustor at a relatively high temperature

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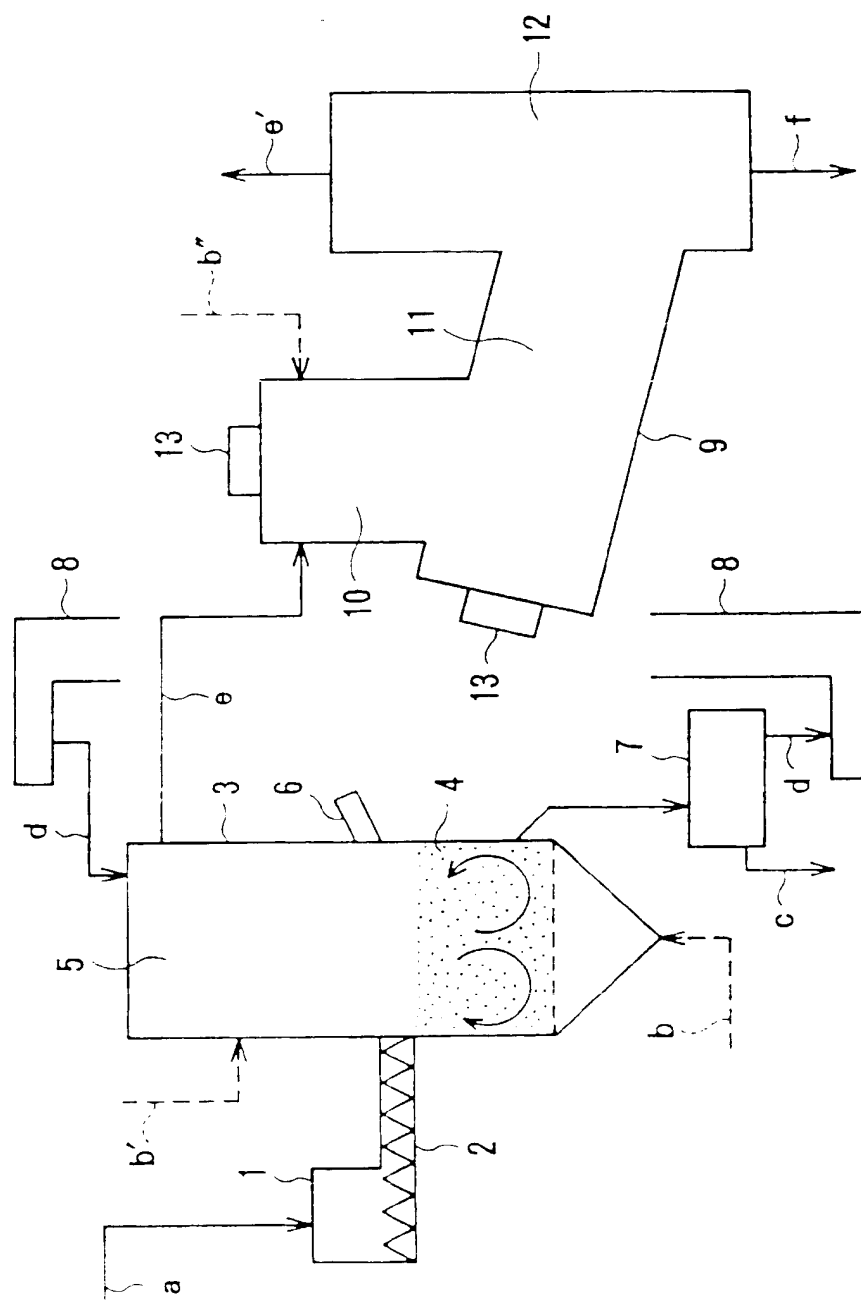
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FIG. 1



F/G.2

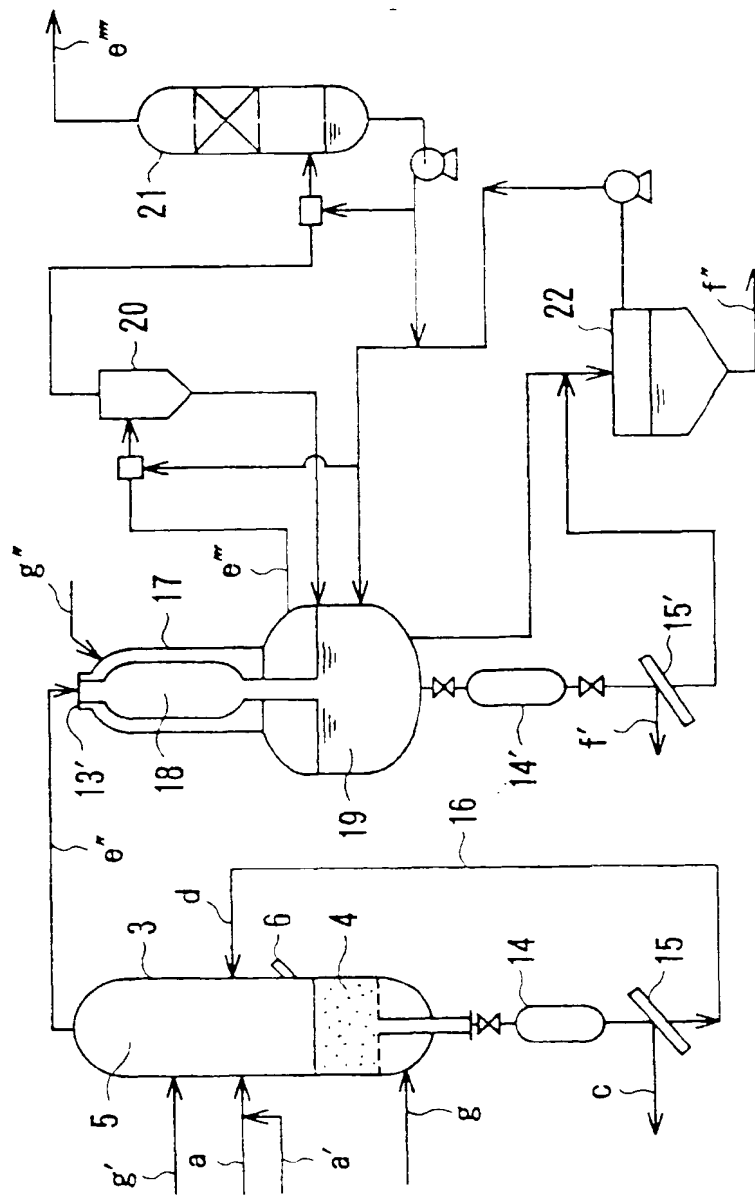


FIG. 3

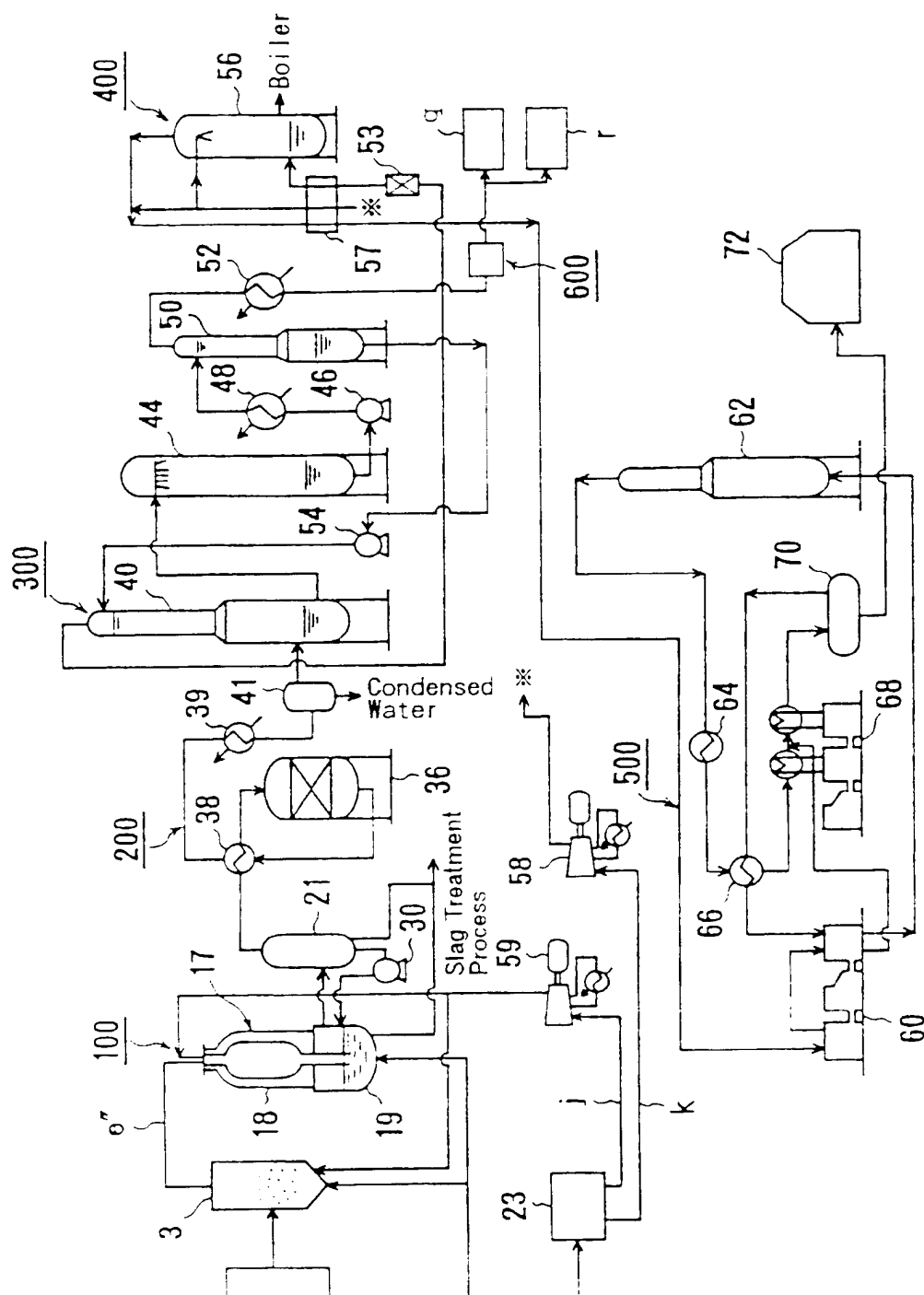
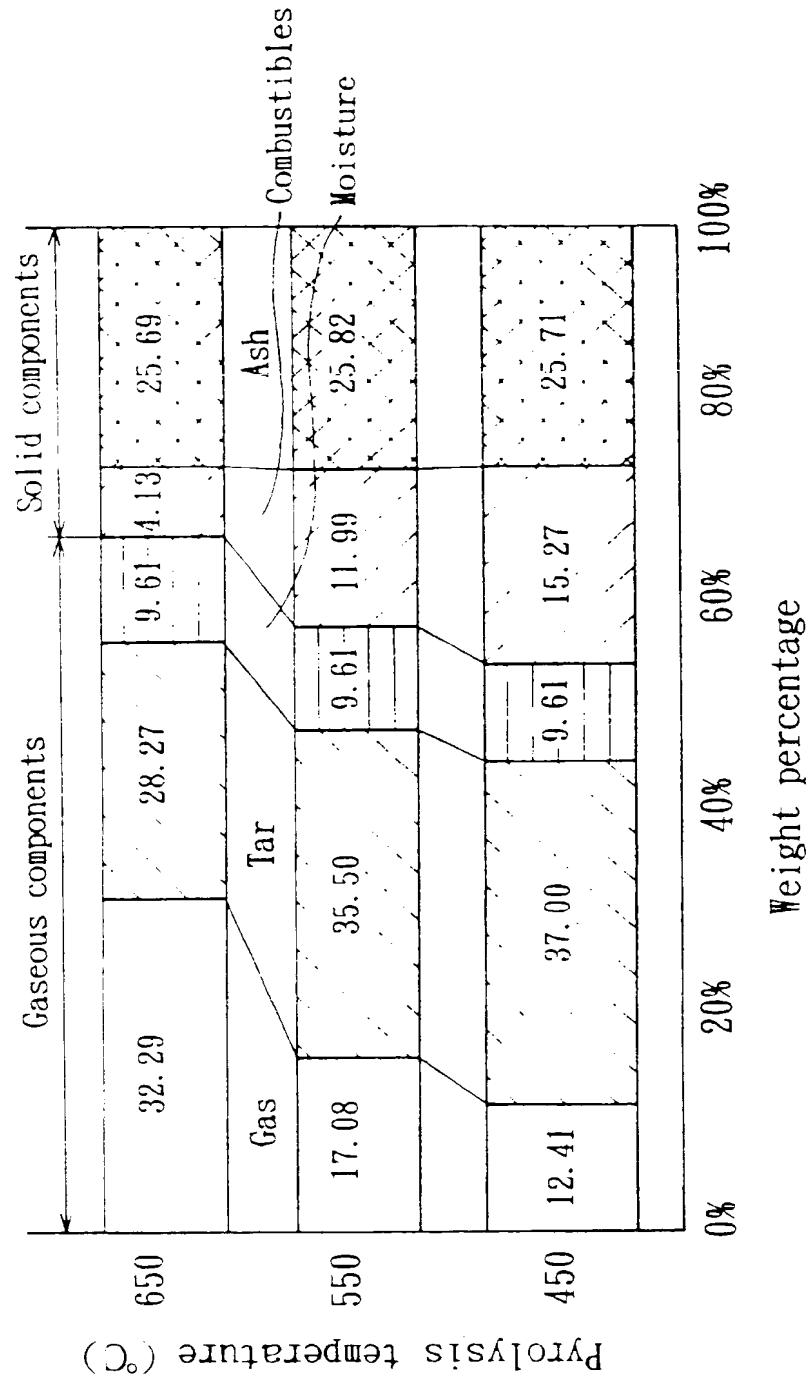


FIG. 4





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 11 9083

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 6)
A	EP 0 153 235 A (FRAMATOME) " IN TOTALITY "	1,5-7,10	C10J3/54 C10J3/56 C10J3/66
A	EP 0 676 465 A (METALLGESELLSCHAFT) * page 2, line 52 - page 3, line 57 *	1,5-7,10	
A	EP 0 676 464 A (EBARA) * page 14-16; claims 1-22 *	1,5-7,10	
A	EP 0 126 961 A (WESTINGHOUSE ELECTR. CO.) * page 3, line 7 - page 4, line 9 *	1,3,4,7,9	
A	US 4 242 458 A (CHILD)		
A	GB 833 551 A (TEXACO)		
P,X	DE 44 35 349 C (NOELL-ENERGIE) 2 May 1996 * column 6, line 29 - column 9, line 27 *	1,4,5,7,10	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 6)
			C10J
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
		20.11.1997	Wenling 1-P

EP 0 803 562 A1

A: technological background
O: non written disclosure
P: intermediate document

A: member of the same patent family, corresponding document

